

REMARKS

The Applicants thank the Examiner for the examination to date and respectfully request reconsideration of the present application in view of the foregoing amendments and the reasons that follow.

Claims 1-25 are currently pending to be examined on their merits.

I. Substance of the Interview

The Applicants appreciate the courtesy extended by Examiner Omgba for conducting an in-person interview on April 6, 2011. During the interview, the U.S. 2006/0149391 (“Opie”) reference was discussed, and the Examiner agreed that Opie should not be a reference based on 35 U.S.C. § 102(b). Also discussed during the interview were the distinctions between conventional crystalline alloys and amorphous alloys; the Examiner acknowledged the distinctions and accordingly agreed to withdraw the statements in the Office Action mailed January 19, 2011 related thereto. Specifically, the Examiner agreed to withdraw the assertions that an amorphous alloy that is mechanically treated would inherently have residual compressive stress that improves the fatigue properties of an amorphous alloy.

II. Claim Rejection – 35 U.S.C. § 102(b)

Claims 1-6 and 8-10 are rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by U.S. Pat. No. 6,638,577 (“Sano”). Claim 7 is rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by U.S. Pat. Pub. No. 2006/0149391 (“Opie.”). The Applicants respectfully traverse the rejections.

Opie Should Be Removed as a Prior Art Reference

At the outset, the Office has acknowledged that Opie should not be a reference under 35 U.S.C. § 102(b), as it has a filing date later than the priority date of the present application. The Office acknowledged during the April 6, 2011 interview that Opie is at most a reference under 35 U.S.C. § 102(e). The Applicants respectfully submit herewith a Katz declaration by Quoc Tran Pham, formerly known as Tranquoc Nguyen, who is a co-inventor of the present

application and Opie. The official document showing the name change (from Tranquoc Nguyen to Quoc Tran Pham) is also submitted herewith as Exhibit A. As stated in the Declaration, the subject matter in the portions of Opie referenced by the Office to reject present claim 7 is not “by another.”

Accordingly, the Applicants respectfully submit that the Pham Declaration has obviated any rejections related to Opie and thus respectfully request that the rejection be withdrawn.

Sano's Teachings Do Not Anticipate the Present Claims

Present independent claims 1, 7, and 8 are not anticipated by Sano's teachings. The Applicants respectfully traverse the Office's rejection both as stated in the Office Action and the Interview Summary mailed April 8, 2011. Specifically, the Applicants respectfully disagree with the Office's apparent reliance on inherency, particularly the Office's characterization that “since Sano was applying shot peening on similar materials as [the] Applicant[s], same results could be expected as a result of applying a similar process to a similar material.” See Interview Summary, Continuation Sheet. As explained below, this characterization is scientifically incorrect, and thus the conclusion derived therefrom is legally erroneous.

An Amorphous Alloy Is Different From a Crystalline Alloy

At the outset, the Applicants reiterate that an amorphous alloy is different from a conventional crystalline alloy, as discussed and agreed upon during the April 6, 2011 Interview. Particularly, the two classes of materials deform very differently. Indeed, as stated throughout the Office Action (*see e.g.*, page 2), a conventional crystalline alloy's durability and fatigue resistance can be improved upon by techniques such as shot-peening. One of ordinary skill in the art can readily appreciate that these techniques can do so because they plastically deform the crystalline alloys, and the plastic deformation in turn produces residual compressive stress in the alloy, which in turn improves durability and fatigue resistance.

However, contrary to the Office's assertion, such a mechanism does **not** take place in an amorphous alloy. One of ordinary skill in the art can readily appreciate that an amorphous alloy is highly elastic and thus does not plastically deform. In fact, one of the references,

WO 97/20601 (“Scruggs”), which is also cited by the Office on page 6 of the Office Action, provides on its page 3 that

“...the amorphous metal sustains very high levels of elastic deformation with **essentially no plastic deformation**. It has been demonstrated that....with essentially **no anelastic or plastic response** of the material.” (Bold emphasis added).

In other words, in contrast to a conventional crystalline alloy, an amorphous alloy that is mechanically treated at the surface does not undergo plastic deformation. Thus, contrary to the Office’s assertion on page 2 of the Office Action, **no** “residual compress stress” is formed in an amorphous alloy, let alone being necessarily present. Thus, in accordance with MPEP § 2112, no inherency is established.

Sano’s Teachings Do Not Anticipate the Present Claims

The distinctions between Sano’s teachings and the present invention go further than the above. At the outset, Sano’s teachings are directed to painting a golf club head by spraying particles onto the club head, which has nothing to do with improving durability and fatigue resistance of the material. The Office appears to be of the position that since Sano was applying shot peening on similar materials as the Applicants, same results could be expected as a result of applying a similar process to a similar material. *See* Interview Summary, Continuation Sheet. This position is incorrect.

The Applicants respectfully remind the Office again that amorphous alloys are distinct from a conventional crystalline alloy and thus a conclusion that might be drawn for the latter is not necessarily true for the former. Merely because the same result could be expected based on results obtained from similar alloys in a crystalline alloy does not mean it is true in amorphous alloys.

The Office’s conclusion that Sano teaches the present invention merely because Sano, merely in passing, mentions the term “amorphous alloy” and the term “shot peening” is tenuous at best. Just because Sano mentions these terms has no bearing on whether Sano’s teachings relate to an amorphous alloy with improved durability and fatigue resistance, as recited in present independent claims 1, 7, and 8. In fact, Sano’s teachings have **nothing** to do with a

method of improving the durability and fatigue resistance of an amorphous alloy, as recited in present independent claim 8. Sano is completely silent in that aspect.

To further illustrate this point, the Applicants submit herewith Exhibit B and respectfully direct the Office's attention to the passage (boxed) in Section II.2.B. Like the amorphous alloys described in the present application, the metallic glass studied in this article is also a zirconium containing amorphous alloy. However, contrary to the Office's assertion, as explicitly stated in the passage, as recent as 2010 (the publication date of Exhibit B), surface modification such as shot peening still does **not** necessarily improve fatigue life of an amorphous alloy, even in a "similar alloy." Thus, the Office's assertion is scientifically incorrect.

Thus, Sano's teachings do not necessarily result in improved durability and fatigue resistance in an article of an amorphous alloy, as recited in present independent claims 1 and 7. Further, Sano's teachings have nothing to do with a method of improving the durability and fatigue resistance of an amorphous alloy, as recited in present independent claim 8. Accordingly, no inherency is established.

Because Sano does not teach each and every element recited in present independent claims 1, 7, and 8, Sano's teachings cannot anticipate present claims 1, 7, and 8, and their respective corresponding dependent claims.

Thus, at least in view of the foregoing, the Applicants respectfully request that the rejections be withdrawn.

III. Claim Rejections – 35 U.S.C. § 103

Claims 11-17 are rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Sano in view of U.S. Pat. Pub. No. 2002/0193177 ("Poynor"). Claims 19-25 are rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Sano in view of U.S. Pat. No. 6,325,868 ("Kim"). Claims 1-5 and 8-10 are, *in the alternative*, rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Sano in view of WO97/20601 ("Scruggs"). Claims 11-17 are rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Sano and Scruggs, and further in view of Poynor. Claims 18-25 are rejected under 35 U.S.C. § 103(a) as allegedly

being unpatentable over Sano and Scruggs, and further in view of Kim. The Applicants respectfully disagree and traverse all of these rejections.

As a preliminary matter, the Applicants note that the U.S. Supreme Court in *KSR Int'l Co. v. Teleflex, Inc.*, 550 U.S. 398 (2007) has not removed the requirement that the prior art reference (or references when combined) must teach or suggest all the claim limitations. Indeed, *KSR* emphasized cases where all features are known. Furthermore, the exemplary rationales listed in MPEP § 2143 suggest that all elements (when the references are combined) need to be known in the art to support a conclusion of obviousness. Thus, the Office is not relieved of its responsibility of finding prior art teaching or suggesting all the features of the claimed invention to establish a *prima facie* case of obviousness.

The Applicants have set forth the distinctions between Sano's teachings and the present invention above. The teachings of Poynor, Kim and Scruggs, alone or in combination, do not at all remedy the deficiencies of Sano's teachings. Thus, one of ordinary skill in the art would not have had a reason to combine the teachings of Sano with those of Poynor, Kim, and Scruggs. Even assuming, *arguendo*, that these teachings were combined, the presently claimed invention would not have resulted.

Therefore, at least in view of the foregoing, the Applicants respectfully request that the rejections be withdrawn.

CONCLUSION

The Applicants believe that the present application is now in condition for allowance and thus respectfully request favorable reconsideration of the application.

The Office is invited to contact the undersigned by telephone if a telephone interview would advance the prosecution of the present application.

The Office is hereby authorized to charge any additional fees which may be required regarding this application, or credit any overpayment, to Deposit Account No. 033975 (Ref. No. 069648-0388438).

Date: April 19, 2011

Respectfully submitted,

/Raj Davé/

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE PATENT Paton *et al.*
APPLICATION OF:
 SERIAL NO.: 10/565,839
 FILING DATE: AUGUST 13, 2004
 ART UNIT: 3726
 CONF. NO. 7755
 EXAMINER ESSAMA OMGBA
 FOR: HIGH DURABILITY STRUCTURES OF AMORPHOUS ALLOY
 AND A METHOD OF FORMING

KATZ DECLARATION BY QUOC TRAN PHAM

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

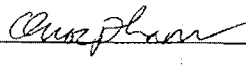
Dear Sir:

I, TRANQUOC NGUYEN, hereby declare as follows:

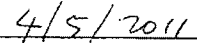
- (1) I am one of the inventors of U.S. Patent Application No. 10/565,839, entitled "HIGH DURABILITY STRUCTURES OF AMORPHOUS ALLOY AND A METHOD OF FORMING " ("the '839 application").
- (2) I have read and am familiar with the Official Action issued by the U.S. Patent and Trademark Office, dated January 19, 2011, in connection with the '839 application.
- (3) I make this declaration in response to the Office Action issued January 19, 2011, in which claim 7 was rejected under 35 U.S.C. §102(e) as being allegedly anticipated by U.S. Pub. No. 2006/0149391 ("Opie").
- (4) The Office has relied on portions of Opie to reject present claim 7. These portions are some disclosures found in Opie in paragraphs [0033] and [0034].
- (5) I am one of the inventors of Opie.

(6) Pursuant to 37 C.F.R. § 1.132, I hereby declare that I am the sole inventor of the subject matter in the portions of Opie relied upon by the Office to reject claim 7 under 35 U.S.C. § 102(e).

(7) I hereby declare that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001 and may jeopardize the validity of the application or any patent issued thereon.



QUOC TRAN PHAM aka TRANQUOC NGUYEN



Date

EXHIBIT A

PETITIONER OR ATTORNEY (Name, state bar number, and address): Tranquoc Thebao Nguyen 2568 W Rome Ave Anaheim, CA 92804		FOR COURT USE ONLY FILED SUPERIOR COURT OF CALIFORNIA COUNTY OF ORANGE LAMOREAUX JUSTICE CENTER NOV 28 2006 ALAN SLATER, Clerk of the Court <i>m. Taylor</i> BY: M. TAYLOR
TELEPHONE NO.: 714-932-4219 FAX NO. (Optional): E-MAIL ADDRESS (Optional): phamax@gmail.com ATTORNEY FOR (Name):		
SUPERIOR COURT OF CALIFORNIA, COUNTY OF ORANGE STREET ADDRESS: MAILING ADDRESS: 341 The City Drive CITY AND ZIP CODE: Orange, CA 92868-3209 BRANCH NAME: Lamoreaux Justice Center (LJC)		
PETITION OF (Names of each petitioners): Tranquoc Thebao Nguyen FOR CHANGE OF NAME		
DECREE CHANGING NAME		CASE NUMBER A239901

1. The petition came regularly for hearing on (date): NOV 28 2006 in Courtroom: 273 of the above-entitled court.

THE COURT FINDS

2. a. All notices required by law have been given.
b. Each person whose name is to be changed identified in item 3 below
(1) ☒ is not ☐ is under the jurisdiction of the Department of Corrections, and
(2) ☒ is not ☐ is required to register as a sex offender under section 290 of the Penal Code.
These determinations were made ☒ by using CLETS/CJIS ☐ based on information provided to the clerk of the court by a local law enforcement agency.
c. ☒ No objections to the proposed change of name were made.
d. ☐ Objections to the proposed change of name were made by (name):

e. It appears to the satisfaction of the court that all the allegations in the petition are true and sufficient and that the petition should be granted.
f. ☐ Other findings (if any):

THE COURT ORDERS

3. The name of
- | <u>Present name</u> | | <u>New name</u> |
|----------------------------------|---------------|-----------------------|
| a. <u>TRANQUOC THEBAO NGUYEN</u> | is changed to | <u>QUOC TRAN PHAM</u> |
| b. _____ | is changed to | _____ |
| c. _____ | is changed to | _____ |
| d. _____ | is changed to | _____ |
| e. _____ | is changed to | _____ |

☐ Additional name changes are listed on Attachment 3.

I hereby certify the foregoing instrument consisting of 1 page(s) is a true and correct copy of the original on file in this court.



ATTEST: (DATE) NOV 28 2006
ALAN SLATER, EXECUTIVE OFFICER AND CLERK OF THE
SUPERIOR COURT OF CALIFORNIA, COUNTY OF ORANGE

BY S. STRAUSS, DEPUTY

Marjorie Laird Carter

NOV 28 2006
JUDGE OF THE SUPERIOR COURT
☐ SIGNATURE OF JUDGE FOLLOWS LAST ATTACHMENT
Marjorie Laird Carter

EXHIBIT B

Understanding the Problem of Fatigue in Bulk Metallic Glasses

J.J. KRUZIC

Early studies suggested there was a severe problem with the fatigue resistance of some bulk metallic glasses (BMGs) and BMG matrix composites, while more recent studies begin to demonstrate a wide variety of fatigue behaviors may be possible for both fully amorphous BMGs and their composites. However, in order to truly understand and control the fatigue behavior of these materials, the role of such factors as thermomechanical processing, the corresponding glass structure, environment, and defects must be understood. Additionally, it is important to understand how these factors relate to the mechanisms of fatigue. This article reviews the current understanding in this regard, and identifies some of the challenges for the future development of fatigue-resistant BMG-based materials.

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I. INTRODUCTION

BULK metallic glasses (BMGs) are a relatively new class of engineering materials with unique and unusual properties that make them potential candidates for many structural applications.^[1] Favorable properties include near theoretical strengths combined with reasonable fracture toughness, low damping, large elastic strain limits, and the ability to be thermoplastically formed into precision-shaped parts with complex geometries,^[2–4] all of which are generally distinct from, or superior to, corresponding crystalline metals and alloys. One property that has been perceived as a limitation for BMGs has been low fatigue resistance relative to crystalline metallic materials; indeed, the first study on $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}$,* the most studied BMG,

*All compositions are given in terms of atomic percent.

found the endurance limit to be only roughly 4 pct of the ultimate tensile strength ($\sigma_{\text{fat}}/\sigma_{\text{UTS}} \approx 0.04$) for four-point bending with a load ratio of $R = P_{\text{min}}/P_{\text{max}} = 0.1$.^[5] However, not all studies to date have been in agreement on this point. The reported 10^7 cycle fatigue strengths for $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}$ vary by a factor of 7,^[5–7] and fatigue thresholds, ΔK_{TH} , vary by a factor of 3.^[5] While some of the reported scatter may be explained by different testing configurations,^[8] this does not account for all the observed variations, for example, those within single studies.^[5,6] Furthermore, a recent review article has shown that when a broad array of Zr-based BMG chemistries are considered, a wide range of fatigue life behavior is observed and many Zr-based BMGs show behavior comparable to crystalline metals

(Figure 1),^[9] suggesting initial concerns may have been specific to certain BMG compositions. Furthermore, while early attempts at making BMG matrix composites also resulted in low fatigue limits and fatigue thresholds,^[10] the latter even worse than comparable fully amorphous BMGs, more recently developed BMG matrix composites demonstrate excellent fatigue resistance.^[11,12]

While it is becoming apparent that it is likely possible to produce BMGs and BMG matrix composites with a rich variety of fatigue properties, the fatigue literature to date has been plagued by a high degree of scatter. Such scatter suggests that some important variables affecting the fatigue behavior of BMGs are not adequately understood or controlled in the experiments. Studies over the last few years have suggested that factors such as the thermal history,^[6,13–15] mechanical history,^[16–18] environment,^[19–22] and defects^[23–25] all may play a role in affecting the fatigue behavior of BMGs. However, most of those factors were rarely characterized, reported, or controlled in early fatigue studies on BMGs, which likely explains some of the reported scatter. Accordingly, the purpose of this article is to review how the preceding factors can affect the measured fatigue behavior of BMGs, identify gaps in the knowledge base, and suggest solutions for making BMG-based materials with both good and repeatable fatigue resistance.

II. VARIABLES AFFECTING FATIGUE BEHAVIOR

A. Thermal History

1. Glass structure and free volume

The free volume is known to be an important factor in determining the mechanical properties of BMGs,^[26–33] a point which has only recently been considered when comparing the fatigue behavior of as-cast amorphous alloys in the absence of hydrogen embrittlement or chemistry changes.^[6] The generally accepted definition

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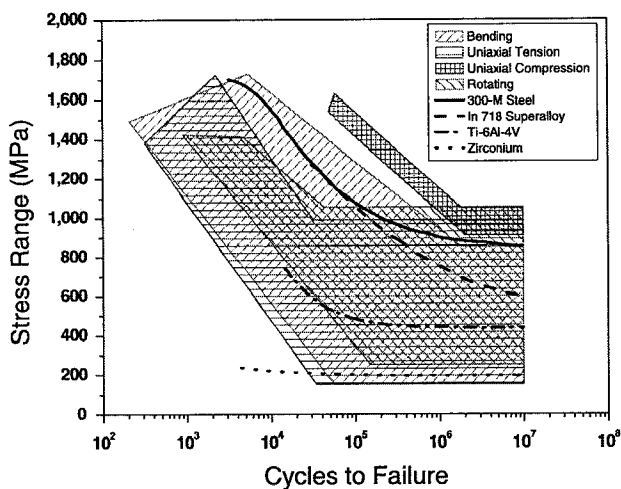


Fig. 1—Ranges of Zr-based BMG fatigue life behavior compared to several engineering alloys. Even in bending, where the worst fatigue performance was originally reported by Gilbert *et al.*,^[5] ratios of fatigue life (stress amplitude) to ultimate tensile strength ($\sigma_{fat}/\sigma_{UTS}$) range as high as 0.25 for certain compositions, which compares favorably with many crystalline alloys. Figure reproduced with permission from Ref. 9.

of free volume is the atomic volume in excess of a fully dense amorphous state, and thus, free volume is widely considered as the open volume sites that allow atoms to flow during deformation. When the free volume of a metallic glass is reduced (*e.g.*, by slow cooling or annealing), deformation and plastic flow is more difficult, the fracture toughness is reduced,^[6,13,26–28,32] and the 10^7 cycle fatigue strength increases.^[6,13] Indeed, the 10^7 cycle fatigue strength was found to vary by a factor of 2 for BMGs of identical composition ($Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$) with different initial free volume states (Figure 2).^[6] In that study, the free volume differences were quantified by thermal analysis using the enthalpy recovery method,^[6,34] and only a marginal reduction in toughness was observed (~ 26 vs $19 \text{ MPa}\sqrt{\text{m}}$). Furthermore, for the similar $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ BMG composition, it has been shown that when the free volume is reduced by structural relaxation *via* sub- T_g annealing, using appropriate times and temperatures to avoid crystallization,^[34] the fatigue crack growth properties are unaffected. This is seen in Figure 3(a), where the fatigue crack growth behavior for samples annealed at 610 K (337 °C) for 1 and 10 times the relaxation time, τ , essentially overlap the curve for samples that have simply been stress relieved. Note, at 10τ , the BMG is essentially fully relaxed and exhibits an order of magnitude drop in fracture toughness from 34 to $3 \text{ MPa}\sqrt{\text{m}}$. Thus, it is surprising that there is negligible effect on the fatigue crack growth behavior. This insensitivity to initial-free volume state has been attributed to the fact that the free volume locally increases at the crack tip due to the intense deformation during fatigue cycling, as determined by depth profiled positron annihilation spectroscopy using the Doppler broadening technique.^[14] Similar results were found for the various samples regardless of the initial free volume state, indicating that in the absence of hydrogen,

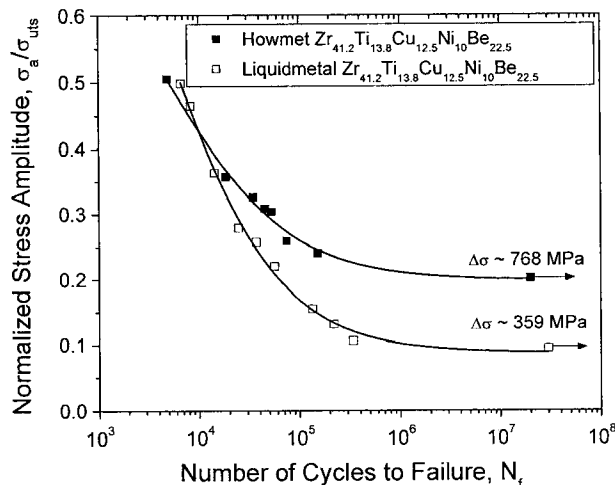


Fig. 2—Plot showing the difference in the 3-point bending fatigue life curves for $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ BMGs produced by different manufacturers with different amounts of free volume. The Howmet produced material, with lower free volume, showed a higher fatigue limit. Figure reproduced with permission from Ref. 6.

the free volume at the fatigue crack tip is determined by the local deformation and not the prior processing history. Finally, such results imply that differences in fatigue life behavior with free volume changes can be attributed to differences in the crack initiation behavior. Indeed, the number of cycles to initiate a crack shows a pronounced effect of free volume, as shown in Figure 3(b).^[13]

In contrast to the preceding results, it has been observed that when free volume is filled with hydrogen, fatigue crack growth is slowed.^[26,27] Such results are not inconsistent with the preceding concept of free volume creation at the crack tip. In the presence of hydrogen, the hydrogen atoms can easily move to fill any new free volume created. Thus, one may conclude that it is not only the amount of free volume, but also the local atomic environment, for example, the presence of hydrogen, that controls fatigue crack growth. Similarly, a study that attempted to affect the free volume of Zr-Cu-Al BMGs by adding 0 to 7 pct Pd found a linear increase in fatigue limit with increasing volume,^[35] which again suggests the chemistry and local atomic environment play a significant role in addition to free volume. Also, it has been shown that not all free volume sites are equivalent and the distribution of different sized sites changes with deformation;^[14,36] thus, different distributions of free volume sizes may influence the behavior as well.

Recent computational studies on model Cu-Zr and Cu-Zr-Al metallic glasses have found that the fraction of icosahedral sites is much more sensitive to changes in cooling rates and structural relaxation than free volume, and those authors suggest that the local (icosahedral) ordering may be a more significant factor for characterizing the structural state of metallic glasses and their mechanical behavior.^[37,38] The role of such short-range ordering on fatigue behavior has yet to be explored; however, generalizing this concept to all metallic glasses may prove difficult. Indeed, it is suggested that

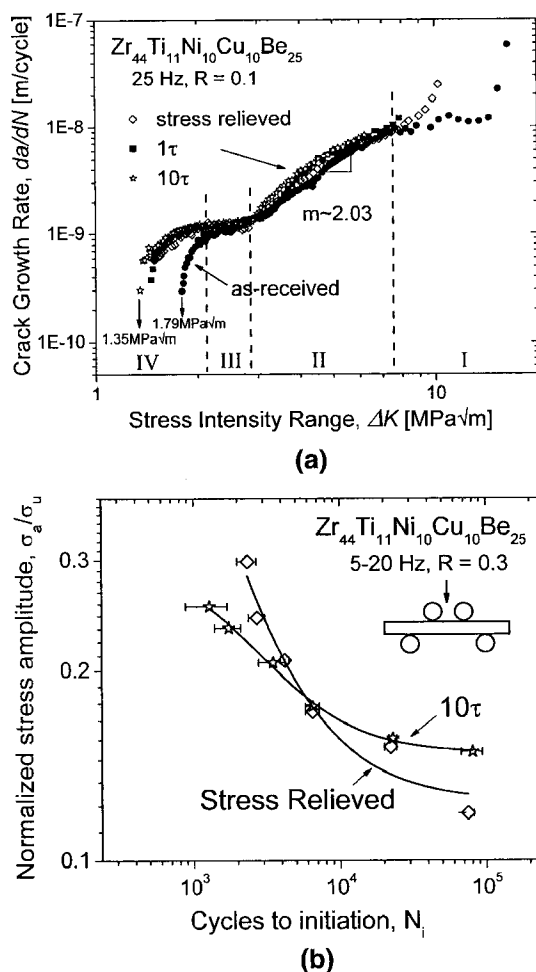


Fig. 3—(a) Plot showing there is no effect of the initial free volume state on the fatigue crack growth behavior for a $\text{Zr}_{44}\text{Ti}_{11}\text{Ni}_{10}\text{Cu}_{10}\text{Be}_{25}$ BMG annealed to three conditions: stress relieved (120 s at 573 K (300 °C)), 1τ (438 s at 610 K (337 °C)), and 10τ (4380 s at 610 K (337 °C)), where τ is the structural relaxation time at 610 K (337 °C). There is, however, an effect of the residual tempering stresses in raising the threshold for the as-received BMG. (b) Plot showing that the number of cycles to crack initiation is affected by the free volume state, as illustrated by comparing the stress-relieved and 10τ conditions. Both figures reproduced with permission from Ref. 13.

icosahedral ordering should not play a role in Al-based glasses.^[39] Overall, one may conclude that a simple model based on the amount of free volume controlling the fatigue properties is likely too simplistic, and various other aspects of the glass structure such as free volume site size and distribution, short and medium range order, as well as hydrogen all likely play a role in determining the fatigue properties.

2. Residual stresses

Residual compressive stresses up to several hundred megapascals may form on the surface of BMGs due to thermal tempering during the casting process.^[40,41] In most literature studies, steps were typically not taken to relieve such stresses prior to fatigue testing. Thus, residual stresses were likely present during fatigue and fracture experiments, potentially affecting the results. Surface compressive stresses are well known to affect the

fracture properties of conventional oxide glasses (*i.e.*, tempered glass), and residual surface stresses caused by shot peening have recently been demonstrated to improve the uniaxial compressive and 3-point bending behavior of BMGs.^[42] Furthermore, recent results show that the fracture and fatigue behavior can indeed be affected by thermal tempering stresses. The fracture toughness, K_{IC} , of a $\text{Zr}_{44}\text{Ti}_{11}\text{Ni}_{10}\text{Cu}_{10}\text{Be}_{25}$ BMG dropped by ~33 pct from 51 to 34 $\text{MPa}\sqrt{\text{m}}$ when the thermal tempering stresses were removed by annealing below the glass transition temperature, T_g .^[13] Similarly, the fatigue threshold, ΔK_{TH} , was found to decrease by ~25 pct from 1.79 to 1.35 $\text{MPa}\sqrt{\text{m}}$, as shown in Figure 3(a).^[13] In that figure, the as-cast samples contained thermal tempering stresses from the casting process, while the stress-relieved samples had the same free volume with no residual stresses. Thermal and structural characterization confirmed that the heat-treated BMG had neither structurally relaxed nor formed nanocrystals.^[13,34] Thus, this provides clear evidence that some of the scatter in the reported fatigue thresholds (*e.g.*, in Reference 5) may be due to residual stresses. This effect is attributed to the compressive residual stresses near the sample surfaces that superimpose on the crack tip stress state, suppressing crack propagation. Fully amorphous BMGs produced with different cooling rates or section thicknesses, or machined from different regions of larger cast plates, may have different residual stresses at the crack tip, affecting the fracture and fatigue properties.

B. Mechanical History

As described in Section II-A-2, surface residual stresses from thermal tempering can have a benefit for both the fracture and fatigue properties of BMGs. Alternatively, a mechanical way to induce surface residual stresses in a material is by shot peening. Shot peening has been demonstrated to be successful in providing compressive residual surface stresses in BMGs and improving the bending and compressive ductility.^[42] However, an initial study on the fatigue behavior

of a shot-peened $\text{Zr}_{21.5}\text{Ti}_{14.2}\text{Cu}_{15.5}\text{Ni}_{14.5}\text{Be}_{3.5}\text{Al}_3$ BMG showed no benefit of shot peening on rotating bending fatigue life.^[17] Instead, crack initiation was found to be shifted ~100 μm below the sample surface, *i.e.*, under the compressive stress layer. It is currently unclear as to the exact reasons why shot peening-induced residual stresses were not beneficial for fatigue of this BMG.

while thermally induced residual stresses do appear beneficial for a $\text{Zr}_{44}\text{Ti}_{11}\text{Ni}_{10}\text{Cu}_{10}\text{Be}_{25}$ BMG in improving both the fatigue threshold and fracture toughness.^[13] However, it is important to note that the shot peening process, in addition to producing residual stresses, concurrently induces large amounts of inhomogeneous deformation into the sample surface region. Inhomogeneous deformation is known to occur by the production of free volume in the metallic glass.^[43] Thus, while the shot-peened layer is under compressive stress, it is also expected to be in a state of higher free volume, which has been found by Launey *et al.* to make crack initiation easier.^[13] Thus, with shot peening, there may

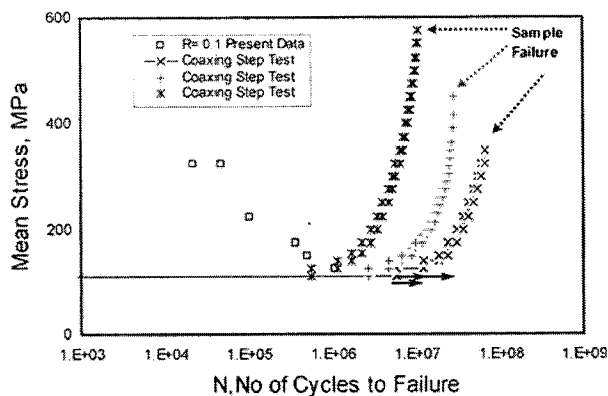


Fig. 4—Plot showing how the mean stress at failure can be coaxed as high as 575 MPa for a $Zr_{41.8}Ti_{12.9}Ni_{9.5}Cu_{12}Be_{23.8}$ BMG by cycling below the fatigue limit. Figure reproduced with permission from Ref. 16.

be competing effects of mechanically altering both the surface stress state and the surface glass structure.

While shot peening has not been demonstrated to improve the fatigue properties to date, conversely, cyclic loading below the fatigue limit has been shown to be beneficial to the fatigue life for a $Zr_{41.8}Ti_{12.9}Ni_{9.5}Cu_{12}Be_{23.8}$ BMG.^[16] Using a fatigue coaxing step test, where the mean stress was increased after each prescribed number of cycles, it was found that the mean stress at failure, which would normally be below 200 MPa, could be increased substantially up to 575 MPa (Figure 4). Thus, even below the fatigue limit, where one might guess little change is occurring in the glass, in fact, significant mechanical changes are induced in the BMG that affect the fatigue behavior. Such results are similar to the findings of Packard *et al.*,^[18] who found a hardening of a $Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$ BMG after cyclically loading with a nanoindenter below the yield point even after a few (≤ 10) cycles. While in both cases the mechanisms are still unclear, these results suggest that the mechanical behavior of BMGs are sensitive to loading history even at very low loading levels. Thus, there are likely potential possibilities for mechanically treating BMGs to tailor fatigue properties that have yet to be explored.

C. Environment

Early studies on $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMGs in aqueous environments found a severe degradation in the fatigue crack growth properties in the presence of NaCl as well as a pronounced stress corrosion cracking effect under static loading.^[20,21] Indeed, the threshold stress intensity range for fatigue crack growth, ΔK_{TH} , was lowered below $1 \text{ MPa}\sqrt{\text{m}}$, and the growth rates at specific ΔK values were found to increase by more than three orders of magnitude. More recent work has shown this corrosion fatigue effect to depend on the NaCl concentration, and also a similar, but less severe, effect was found for aqueous solutions containing $NaClO_4$ or $NaSO_4$.^[22] Those authors attributed the poor environmental cracking resistance of that BMG primarily to its

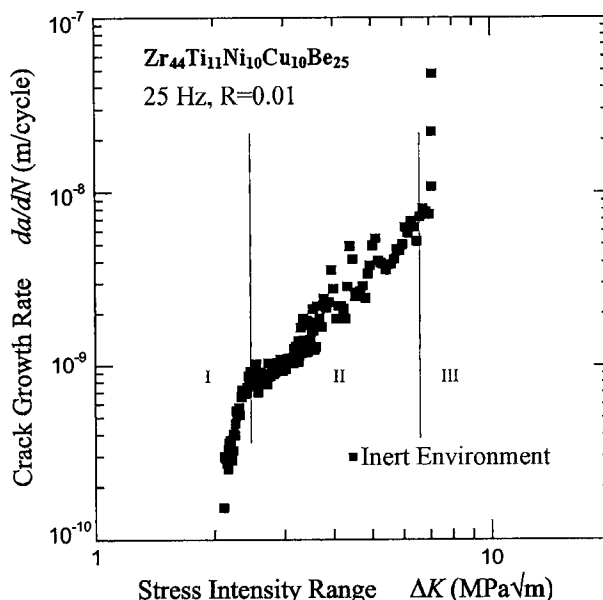


Fig. 5—Plot showing the fatigue crack growth curve of a $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ BMG tested in dry flowing N_2 gas. When compared to Fig. 3(a), the fatigue threshold is higher and the plateau region at 10^{-9} m/cycle is gone when testing is conducted in an inert environment. Figure reproduced with permission from Ref. 19.

chemical composition, which does not give a strongly protective oxide at the crack tip.

Fatigue crack growth data collected in ambient room air for $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ and $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ bulk metallic glasses (BMGs) found in the literature often display a plateau in the crack growth curve at around 10^{-9} m/cycle , where the growth rate is relatively insensitive to the applied stress intensity range^[13,44] (Figure 3(a)). In the fatigue of materials, such behavior generally indicates that something other than mechanical loading acts as the rate limiting step in the crack growth process, and that commonly is an interaction with the environment.^[45-47] A $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ BMG, when tested in dry inert atmosphere, exhibits a significantly higher fatigue threshold, ΔK_{TH} , and a characteristic three-region fatigue curve, as seen in Figure 5.^[19] The plateau in the crack growth curve near $\sim 10^{-9} \text{ m/cycle}$, seen in Figure 3(a), is not present in the fatigue curve measured in purified dry N_2 , indicating that the fatigue behavior is degraded by the ambient air environment. Furthermore, changing the alloy chemistry can profoundly influence this effect. Recent studies on a $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ BMG showed that the plateau crack growth rates shift to a ~ 25 times higher growth rate.^[48] Furthermore, fatigue life experiments on Zr-Al-Cu and Zr-Al-Cu-Ni BMGs have shown no discernable difference in the S/N curves and fatigue limits for samples tested in air and vacuum.^[49] While it is difficult to make direct links between the fatigue limit and fatigue threshold since the former is affected by both crack initiation and growth, such observations indicate that not all BMGs should be expected to have a similar degrading environmental effect on the fatigue behavior in ambient air.

Furthermore, it is interesting to note that not all studies on $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ BMGs have observed such a plateau for tests conducted in air or even deionized water, *e.g.*, References 5, 20–22, and 50. This suggests that the extreme environmental sensitivity of this composition in air may not be a simple matter of the presence of water vapor or oxygen. There is clearly much to be understood about the environmental effects on the fatigue behavior of Zr-based BMGs, including the specific role of various environmental species, the mechanisms of attack at the crack tip, and the role of specific elements in the various BMG compositions.

Environmental interactions such as oxidation and hydrogen embrittlement for metallic glasses have been documented in the literature,^[26,27,51–61] and either could provide possible mechanisms that could affect fatigue crack growth rates in ambient air.^[19] Interestingly, studies on hydrogen-charged $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ have actually shown a decrease in fatigue crack growth rates and an increase in the fatigue threshold with increasing hydrogen charging (Figure 6).^[26] This suggests that hydrogen may retard fatigue crack growth, which was attributed to a combination of (1) roughness-induced crack closure and (2) the filling of free volume causing a change in the plastic flow behavior. Extensive hydrogen charging caused a very tortuous crack path, causing significant crack closure. However, uncharged samples tested in air show a straight crack path in both References 13 and 44 similar to the samples tested in inert atmosphere.^[19] Thus, roughness-induced crack closure does not seem to be an important mechanism without hydrogen charging. Suh and Dauskardt pointed out that the overall fatigue crack behavior of hydrogen-charged $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ results from a

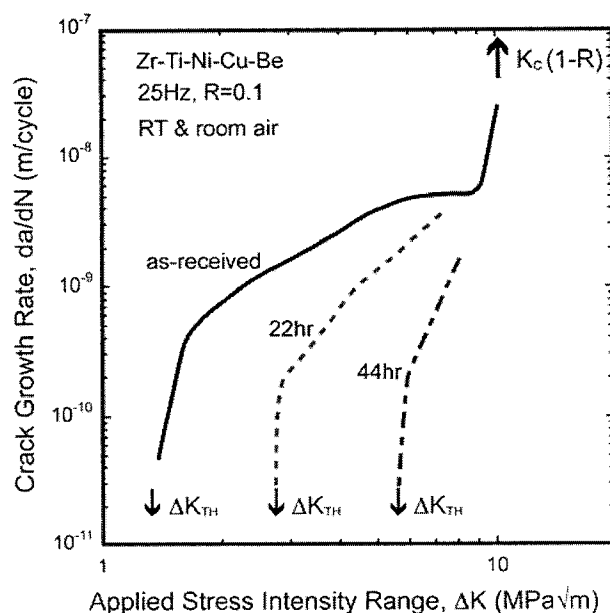


Fig. 6—Plot showing the effect of decreased fatigue crack growth rates and increased fatigue thresholds, ΔK_{TH} , with hydrogen charging. The solid curve represents no charging, the dotted curve 22 h of hydrogen charging, and the dash-dotted curve 44 h of hydrogen charging. Figure reproduced based on data from Ref. 26.

mutual competition of intrinsic embrittling mechanisms and extrinsic shielding mechanisms.^[26] Thus, without hydrogen charging, small amounts of hydrogen entering the crack tip, perhaps from oxidation reactions with water vapor, may cause the material to behave drastically different than a BMG that was heavily hydrogen charged. In other words, the balance of this competition may be shifted under different conditions of hydrogen exposure.

D. Defects

Defects are invariably present in all materials, and BMGs are no exceptions. Defects that may aid in initiating fatigue cracks include voids, inclusions, surface scratches, quasi-crystals, as well as metastable and stable crystallites. Although defects in BMGs are usually quite small, BMG processing is not as well developed as traditional metal processing, and occasionally large defects are found even in commercial materials (Figure 7). In experimentally produced alloys, the possibility for unwanted defects is present as well, *e.g.*, as in Reference 48.

With regard to fatigue behavior, studies on crack initiation in $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}$ BMGs have often reported that (1) cracks initiate at defects and (2) crack initiation is almost instantaneous upon fatigue cycling.^[23–25] In those articles, it is argued that if defects can be reduced or eliminated, there should be a positive benefit for the fatigue life. Indeed, a study on a $\text{Zr}_{44}\text{Ti}_{11}\text{Ni}_{10}\text{Cu}_{10}\text{Be}_{25}$ BMG found crack initiation to only occur after 10^3 to 10^5 cycles and that the amount of cycles needed to initiate cracks could be affected by sub- T_g annealing,^[13] as discussed in Section II-A-1. Also, a different study on a $\text{Zr}_{41.8}\text{Ti}_{12.9}\text{Ni}_{9.5}\text{Cu}_{12}\text{Be}_{23.8}$ BMG suggests that the crack initiation process was not instantaneous for their material and may be affected by precycling below the fatigue limit, as discussed in Section II-B.^[16] Such results suggest that instantaneous crack initiation is not an inherent trait of BMGs and may only occur in materials with a large defect

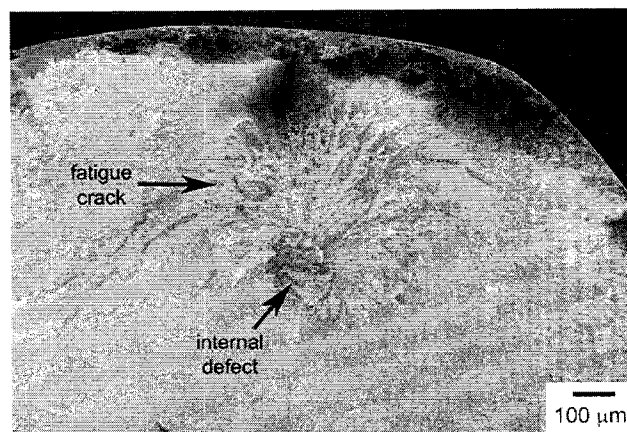


Fig. 7—Example of a fatigue failure that originated at a large internal defect in a commercially produced BMG. Photo courtesy of Dr. Maximilien Launey.

population, unfavorable residual stresses, or unfavorable glass structure or chemistry.

III. STRATEGIES FOR IMPROVING FATIGUE BEHAVIOR

One recent proposed strategy to produce fatigue-resistant materials with tensile strengths similar to BMGs is to create semicrystalline BMG matrix composite materials based on the Zr-Ti-Nb-Cu-Be system.^[11,12] Compared to the best fully amorphous Zr-based BMG tested in four-point bending where the ratio of fatigue life (stress amplitude) to ultimate tensile strength is $\sigma_{\text{fat}}/\sigma_{\text{UTS}} = 0.25$,^[62] these composites have an even higher ratio of 0.3, also measured in four-point bending.^[11] While this composite approach has produced some materials with fantastic strength, toughness, tensile ductility, and fatigue properties, one should be careful before assuming it is a universal solution to fatigue problems. Indeed, early Zr-Ti-Nb-Cu-Ni-Be BMG matrix composites actually showed worse fatigue crack growth properties compared to many fully amorphous BMGs and fairly poor fatigue life properties.^[10] The recent studies argue that the improvement in fatigue properties is the result of a refinement of the size scale of the crystalline phase spacing; however, to date, it is unclear if this is the main or only cause for the difference in behavior. Indeed, composites with a BMG matrix phase are likely to have at least some susceptibility to the variables discussed previously, including free volume and structure of the glass matrix phase, residual stresses, environmental attack, and defects. Furthermore, it is not clear if such composites will be able to take advantage of all of the recent advances in BMG processing,^[63-67] and while fully amorphous BMGs might never achieve the fatigue resistance of BMG matrix composites, it has been shown that some compositions can have fatigue resistance comparable to many fully crystalline alloys (Figure 1).^[9] Thus, fatigue studies need to continue for fully amorphous BMGs both as materials of interest for many applications and as a phase which will in part control the fatigue properties of BMG matrix composite materials.

More general solutions to the problems of fatigue in BMGs and BMG matrix composites will require a fundamental understanding of the variables and mechanisms that control the fatigue behavior of BMGs. Some potential strategies include the following.

- (1) *Develop compositions resistant to environmental attack.* It is known that the Zr-Ti-Ni-Cu-Be BMG compositions are particularly bad in this regard,^[19-22] which likely contributed to the very low fatigue limit observed by Gilbert *et al.*^[5] and the overall bad reputation of BMGs for poor fatigue resistance. While there is in fact a large range of fatigue life behavior seen for different Zr-based BMG compositions^[9] and some results suggest that not all Zr-based compositions exhibit an environmental effect in air,^[49] the mechanisms for the environmental attack are poorly understood, and

thus science-driven strategies for designing BMGs to resist it are unknown at this point. Furthermore, very little is known about non-Zr-based compositions. Clearly, there are many potential BMG compositions to be examined that may not exhibit such detrimental environmental effects, but a fundamental understanding of the mechanisms involved will be needed to drive this pursuit.

- (2) *Better control of thermomechanical processing.* As with crystalline metals, it is clear that the thermomechanical processing can vastly alter the mechanical behavior of BMGs by changing the amount of free volume, the glass structure, the residual stresses, *etc.* However, controlling these factors is challenging, because there are few techniques available for taking a snapshot of the free volume, glass structure, or residual stresses as can be done with crystalline materials using traditional microscopy and diffraction methods. For example, quantifying free volume generally involves relative measurements where the initial reference state is poorly characterized in an absolute sense,^[14,34,36,68] while methods for investigating medium range order are in their early development stages.^[69] Further development of characterization techniques will certainly help in this area, especially when there is much still to be understood about the mechanisms of many observed thermomechanical phenomena affecting fatigue behavior.^[6,13-18]
- (3) *Better control of defects.* It has been well documented that fatigue cracks can initiate at defects in BMGs even after only a few fatigue cycles,^[23-25] although not all studies have observed such rapid crack initiation.^[13,16] Several strategies might be employed to mitigate such effects. Eliminating defects is likely one effective strategy; for example, an arc furnace with tilt casting has been used to make crystalline inclusion-free BMGs for fatigue studies.^[35] However, eliminating defects is likely not always practical for scaling up in an industrial setting. Alternatively, there may be strategies available for suppressing crack initiation and the role of defects, including thermomechanical treatments.^[6,13,16] Again, further understanding of the mechanisms of fatigue and the interactions between defects, thermomechanical treatments, and environment will be needed to allow the development of strategies for preventing premature fatigue crack initiation.

IV. SUMMARY

Similar to crystalline metals, the mechanical properties of BMGs are sensitive to many factors, including thermomechanical processing, the corresponding glass structure, environment, and defects. In order to truly understand and control the fatigue behavior of BMGs and BMG matrix composites, the role of such factors, and the mechanisms involved, must be understood. Unfortunately, there are many challenges in this regard. Unlike crystalline materials, which are easily characterized

by microscopy and diffraction methods, characterization of BMGs is quite challenging, especially with regard to glass structure, free volume, residual stresses, etc. Thus, solving problems of fatigue behavior in BMGs will require both further studies on fatigue mechanisms as well as further developments in characterization tools for BMGs.

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